

## **Supporting Information**

### **Functionalization of Nine-Atom Deltahedral Zintl Ions with Organic Substituents: Detailed Studies of the Reactions**

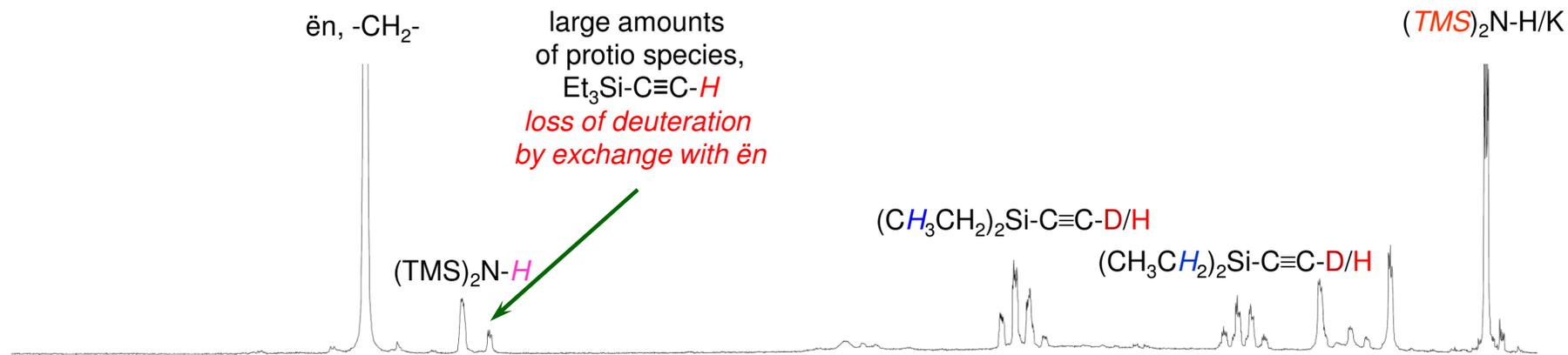
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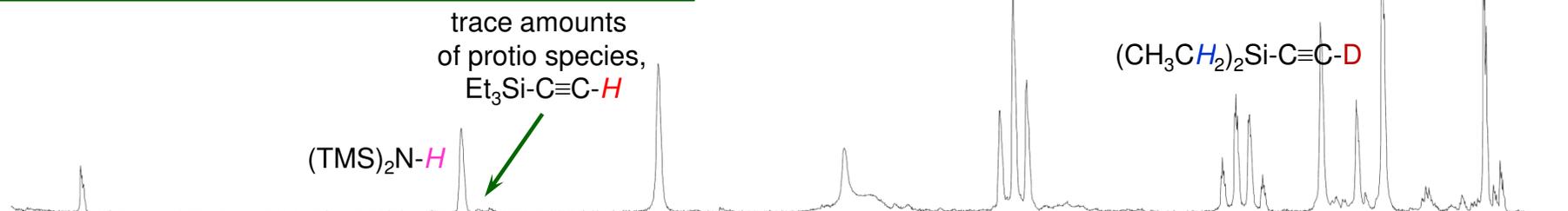
*ssevov@nd.edu*



Exchange of Alkyne Deuterium:



Deuteration of Alkyne:



Formation of Alkyne:

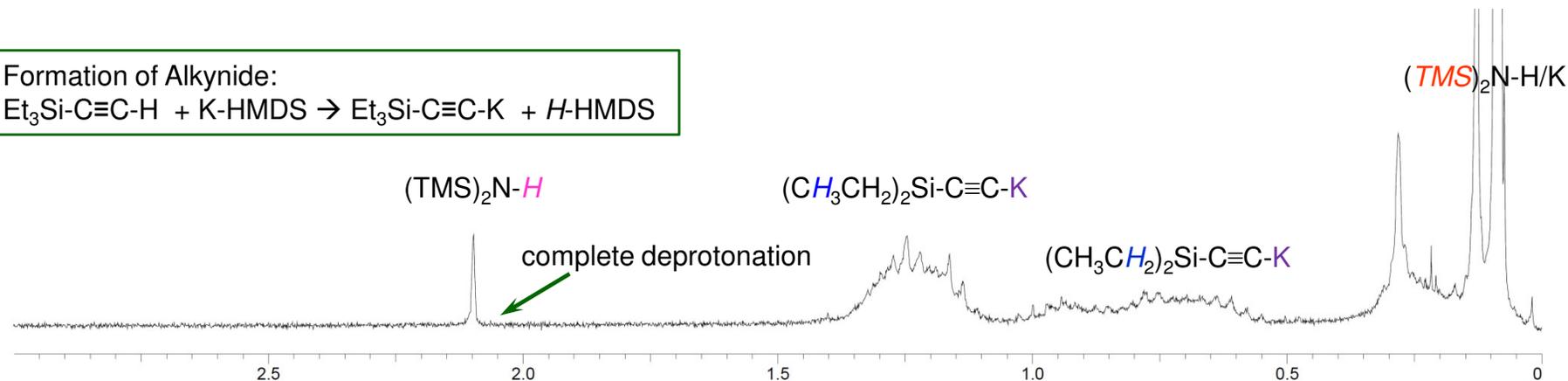


Figure S2 <sup>1</sup>H NMR Deuteration and Exchange with Ethylenediamine

S4

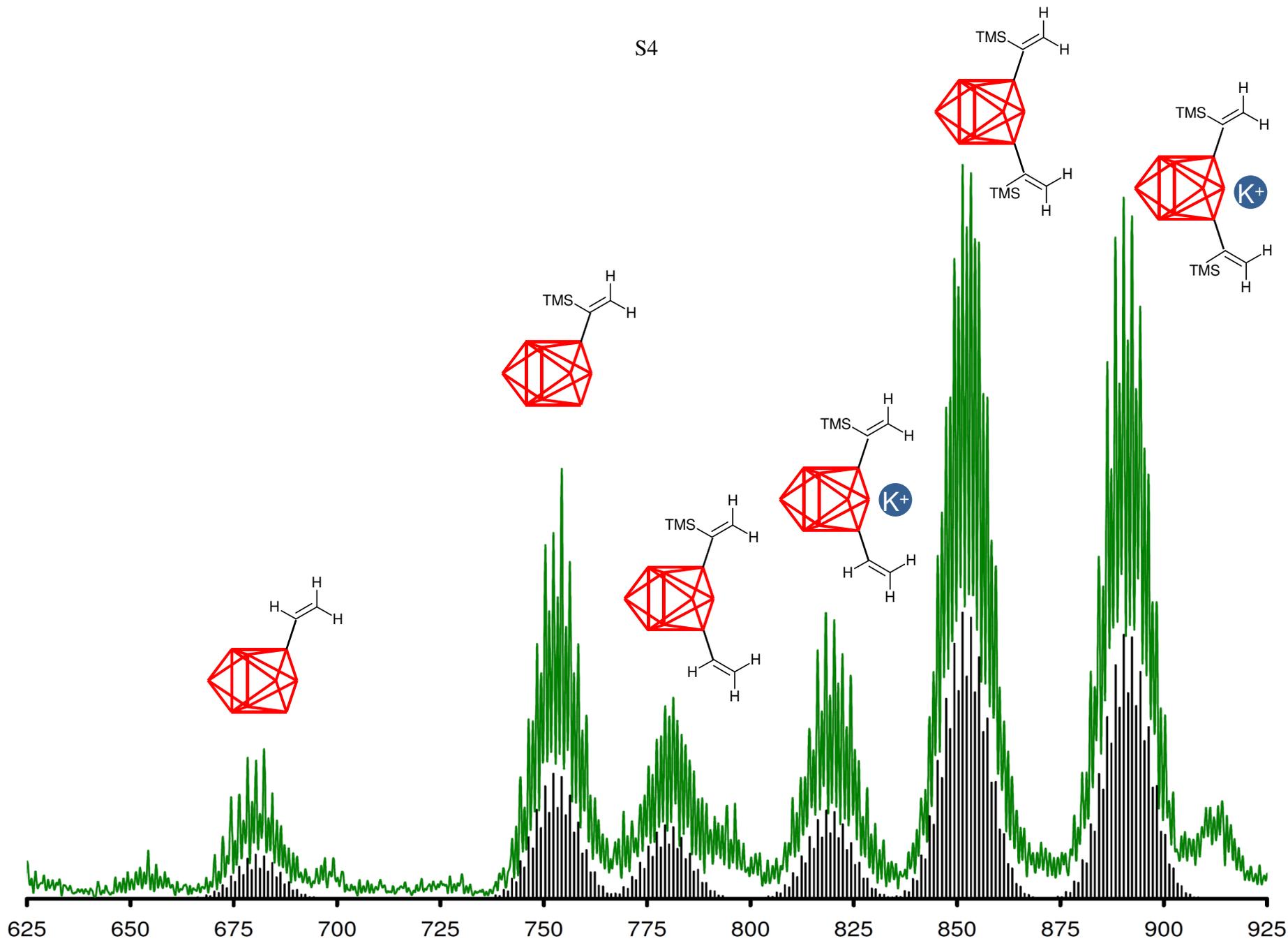


Figure S3 ES-MS of the reaction of  $\text{Ge}_9^{n-}$  with  $\text{TMS-C}(\text{Br})=\text{CH}_2$

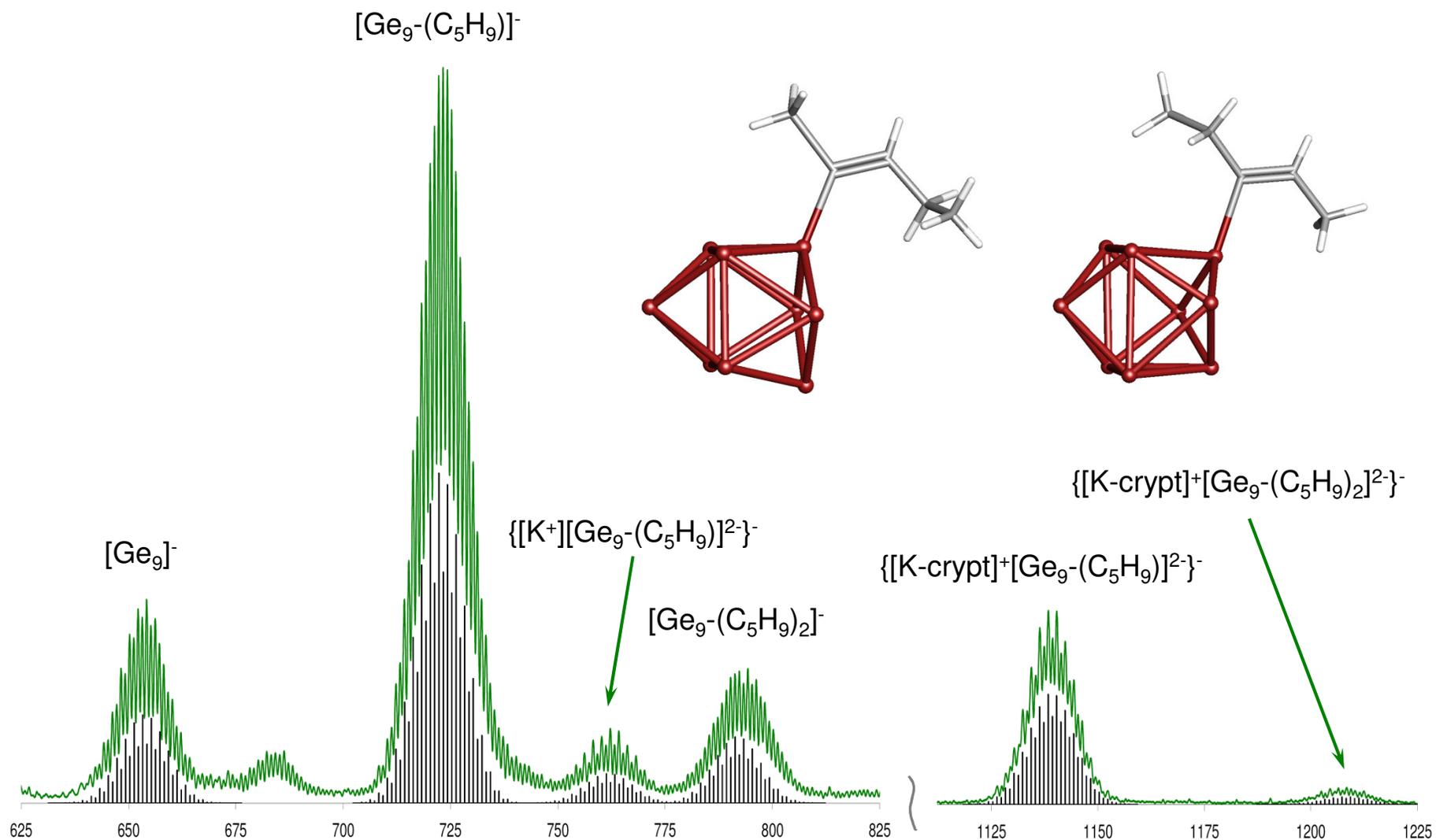


Figure S4 ES-MS of  $[\text{K-crypt}]_3[\text{Ge}_9-(\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2\text{CH}_3)]_{0.5}[\text{Ge}_9-(\text{C}(\text{CH}_2\text{CH}_3)=\text{CHCH}_3)]_{0.5}$

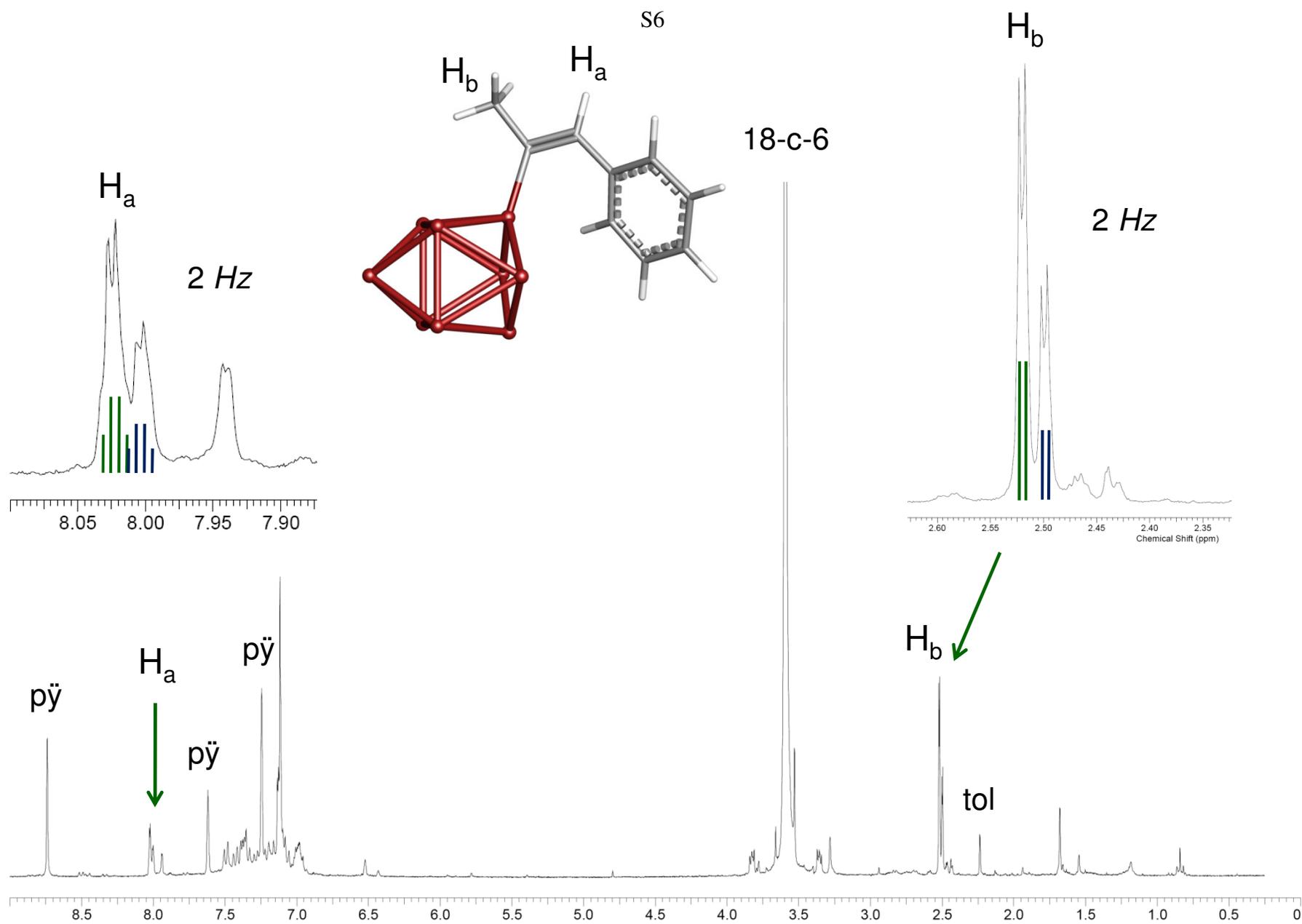


Figure S5  $^1\text{H}$  NMR of  $[\text{K-crown}]_{4-n}[\text{Ge}_9-(\text{C}(\text{Me})=\text{CH}-\text{Ph})_n]$  ( $n = 1, 2$ ) in  $d_5$ -pyridine

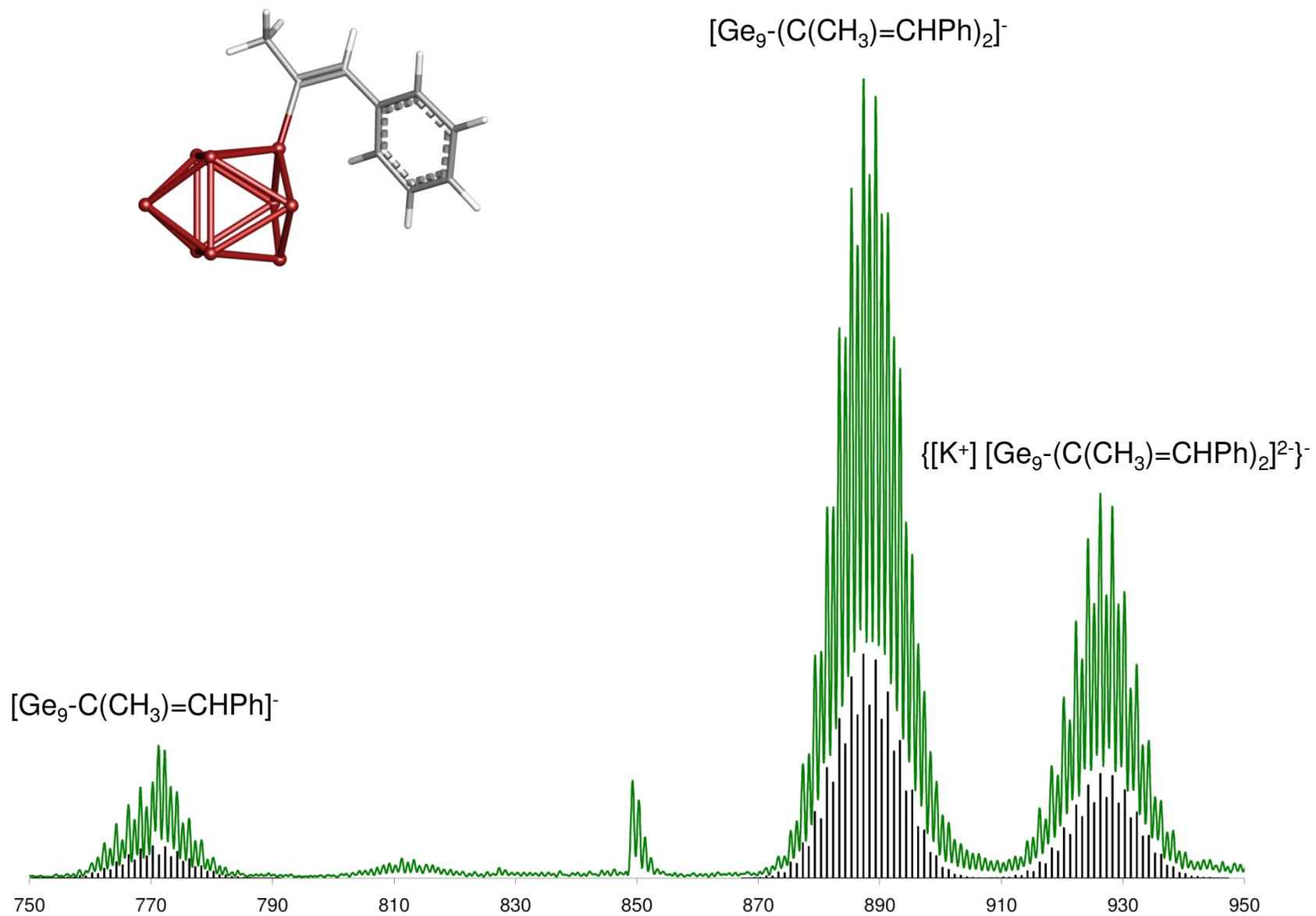


Figure S6 ES-MS of  $[\text{Ge}_9-(\text{C}(\text{CH}_3)=\text{CHPh})_{1,2}]^{n-}$  in ethylenediamine

S8

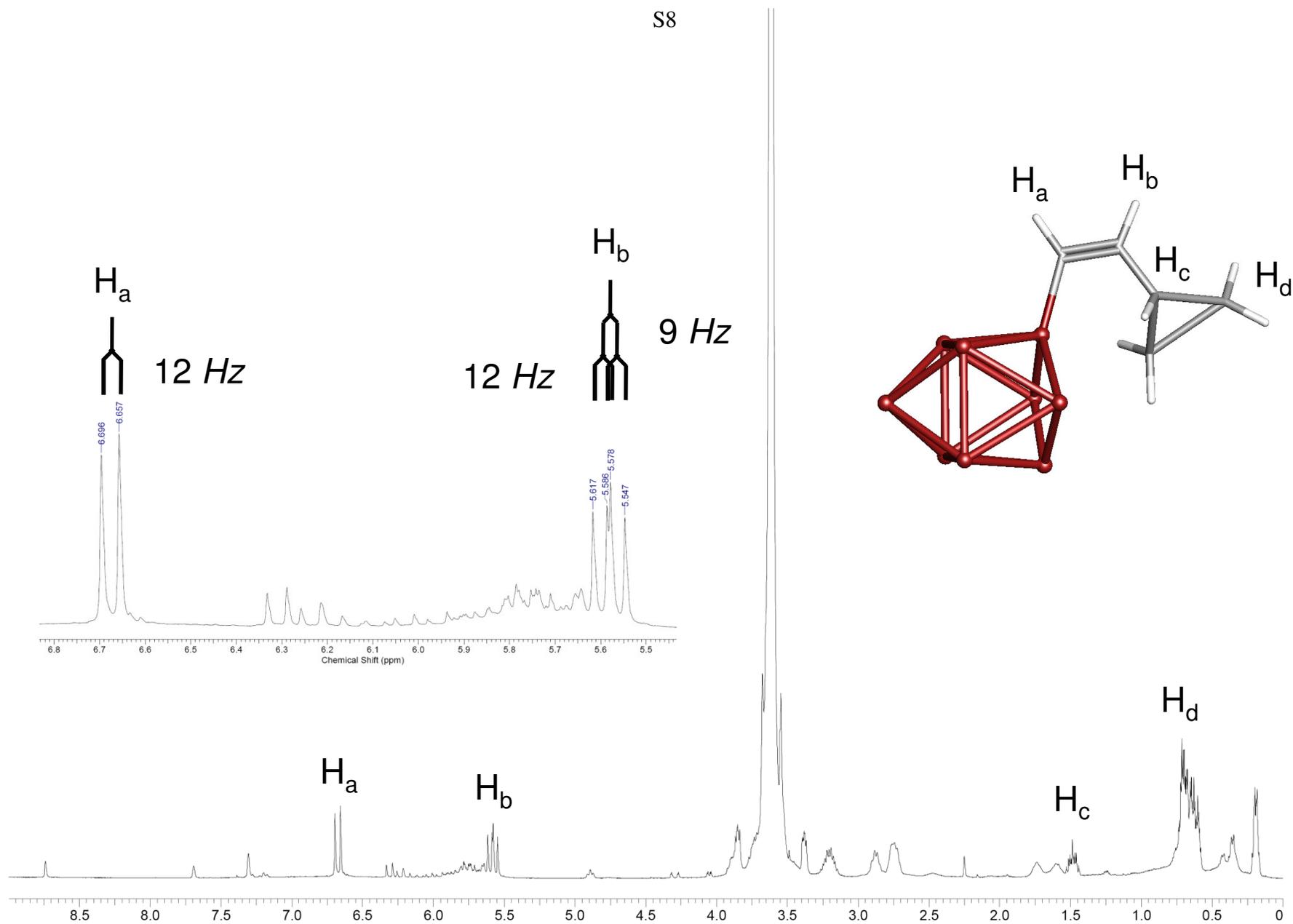


Figure S7  $^1\text{H}$  NMR of  $[\text{K-crown}]_2[\text{Ge}_9-(\text{CH}=\text{CH}-\text{CH}(\text{CH}_2)_2)_2]$  in  $d_5$ -pyridine

S9

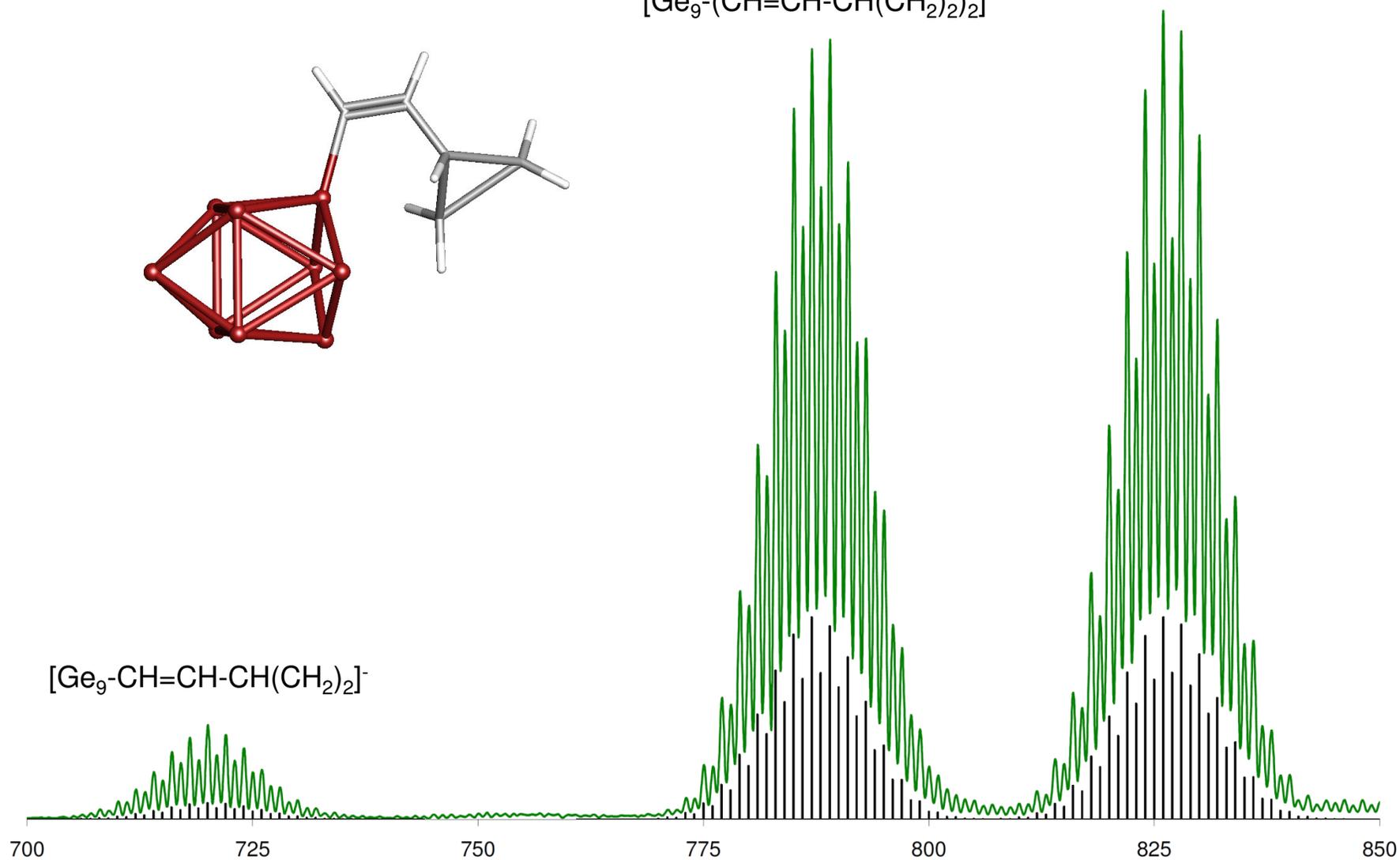
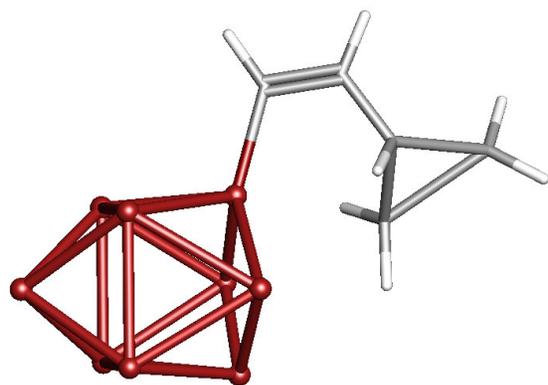
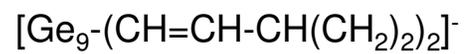
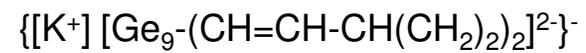


Figure S8 ES-MS of  $[Ge_9-(CH=CH-CH_2CH(CH_2)_2)_{1,2}]^{n-}$  in ethylenediamine

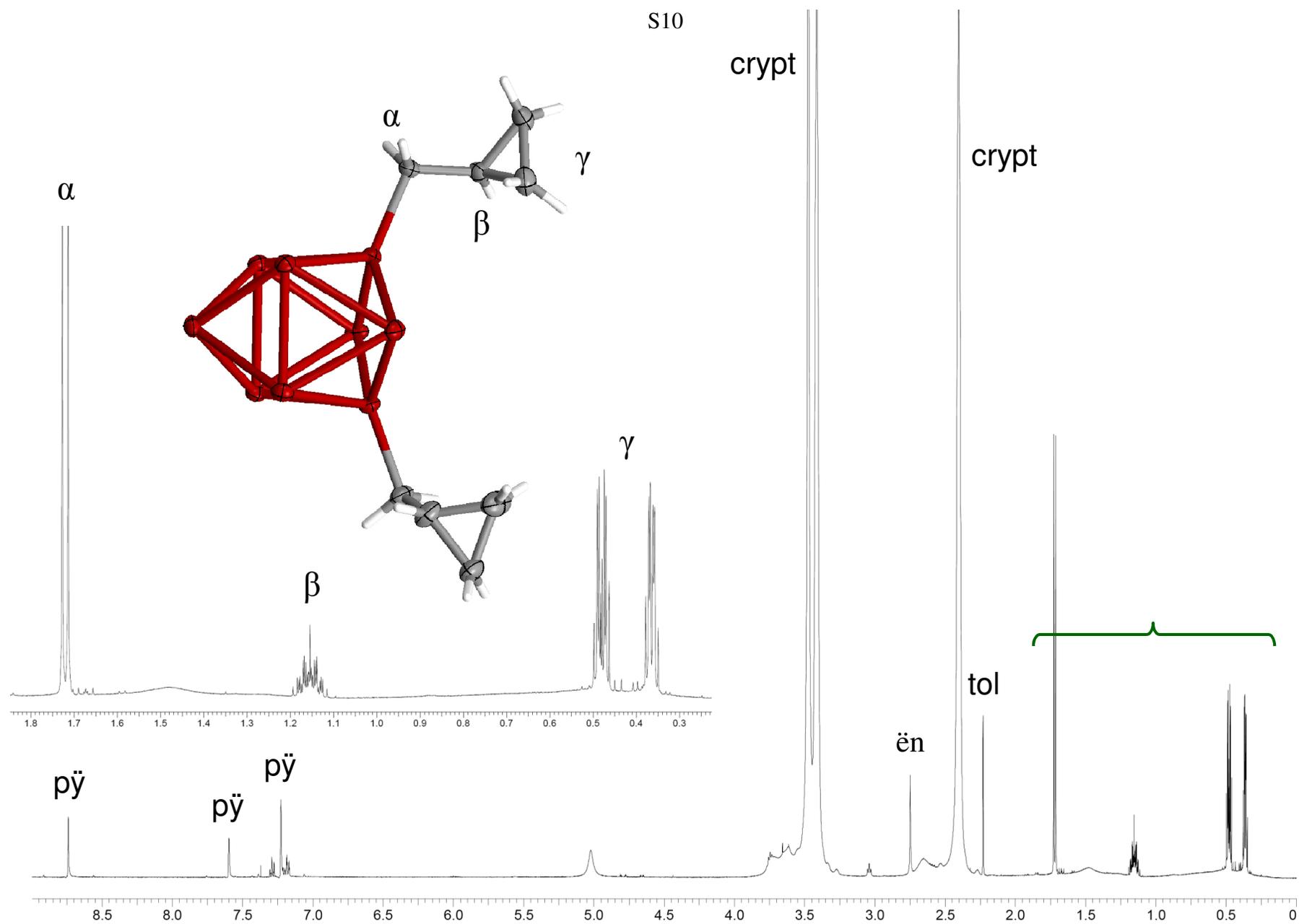


Figure S9  $^1\text{H}$  NMR of  $[\text{K-crypt}]_2[\text{Ge}_9-(\text{CH}_2\text{CH}(\text{CH}_2)_2)_2]$  in  $\text{d}_5$ -pyridine

S11

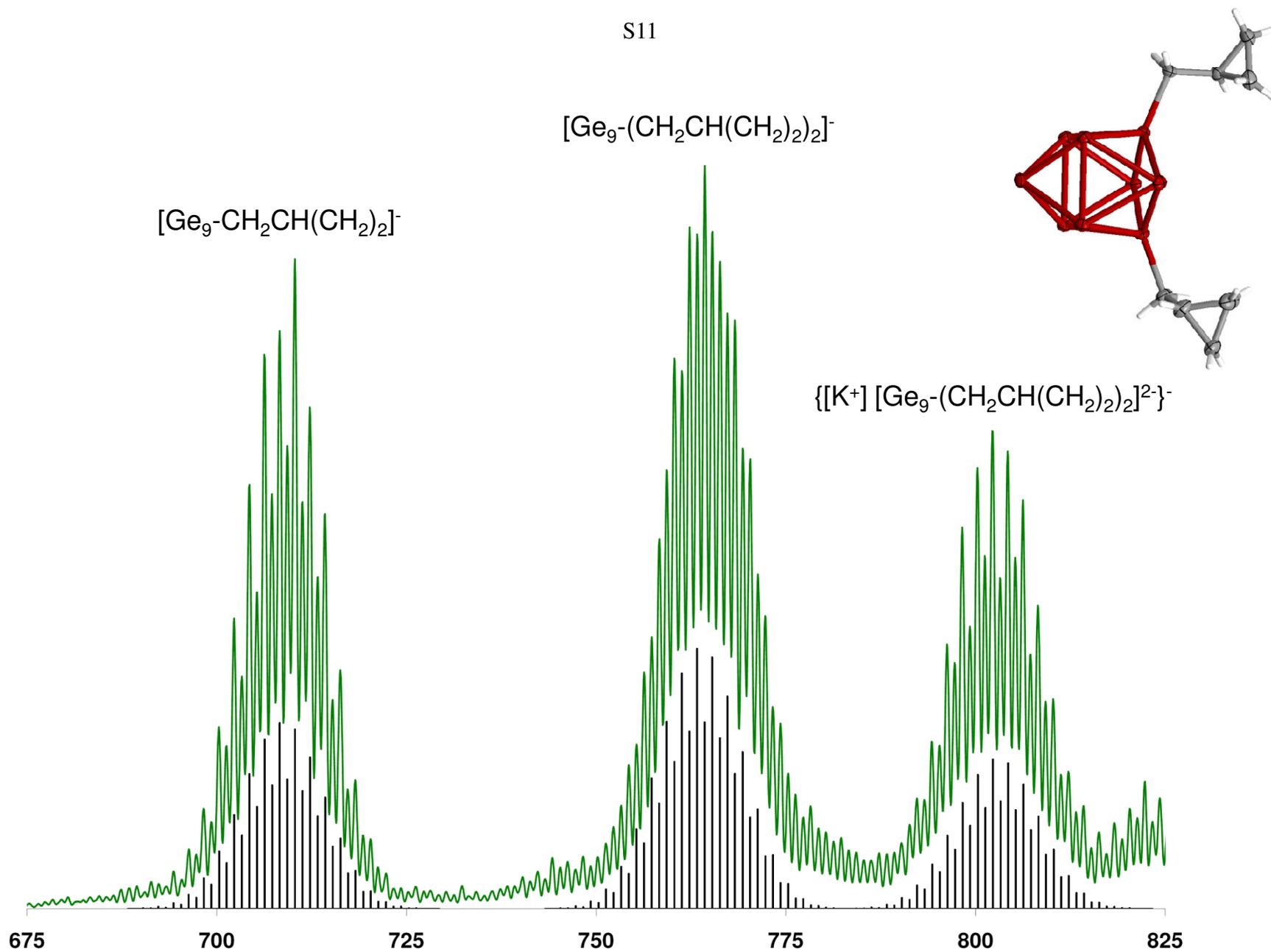


Figure S10 ES-MS of  $[\text{Ge}_9-(\text{CH}_2\text{CH}(\text{CH}_2)_2)_{1,2}]^{n-}$  in ethylenediamine